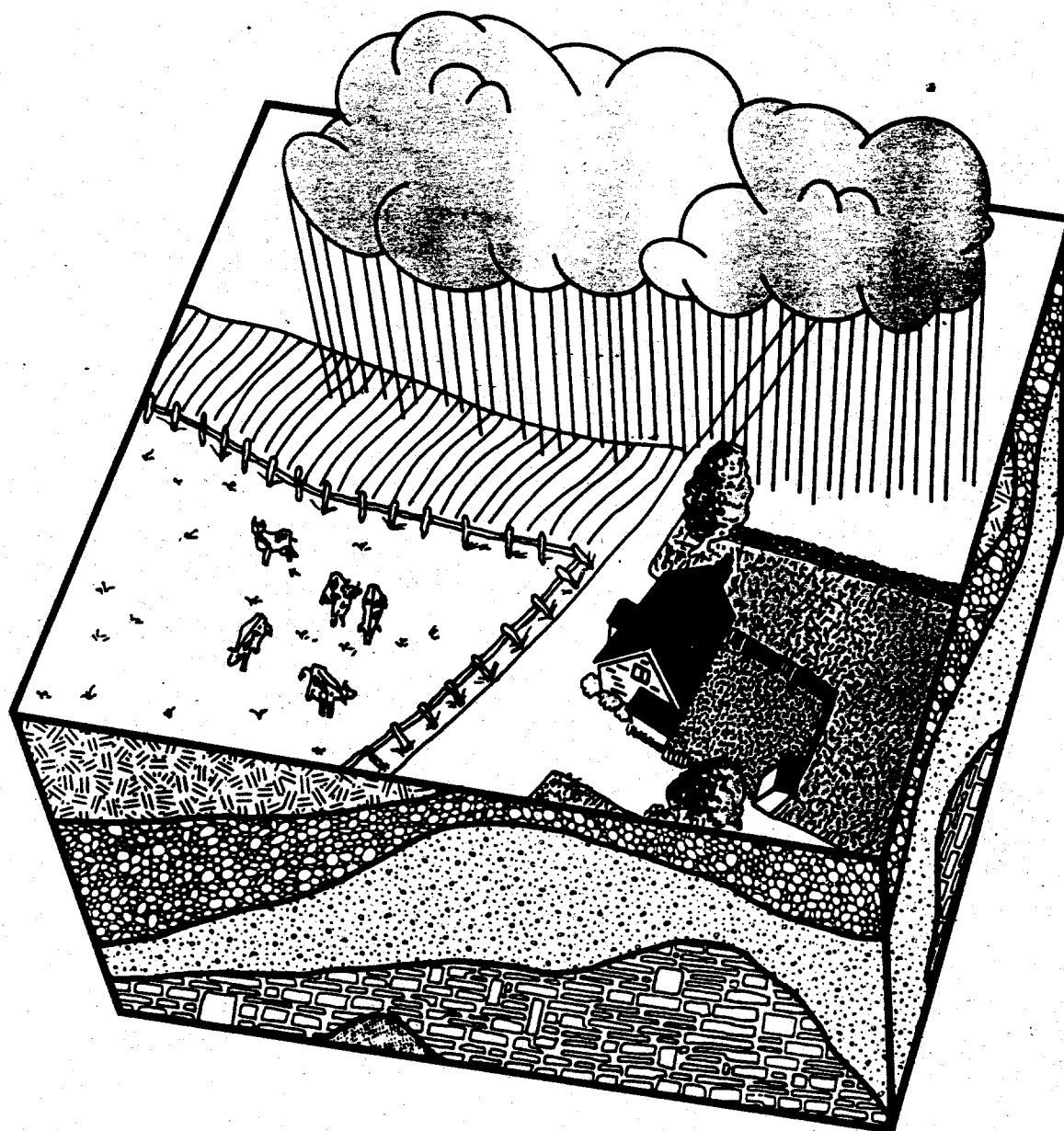




# Hazard Evaluation Division Standard Evaluation Procedure

## Aerobic Soil Metabolism Studies

### Support Document 43



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HAZARD EVALUATION DIVISION  
STANDARD EVALUATION PROCEDURE  
AEROBIC SOIL METABOLISM STUDIES

Prepared by

Clinton L. Fletcher  
Samuel M. Creeger

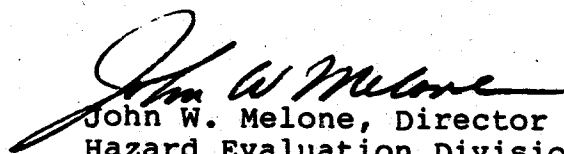
Standard Evaluation Procedures Project Manager  
Stephen L. Johnson  
Hazard Evaluation Division  
Office of Pesticide Programs

United States Environmental Protection Agency  
Office of Pesticide Programs  
Washington, D.C. 20460

## STANDARD EVALUATION PROCEDURE

### PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.

  
John W. Melone, Director  
Hazard Evaluation Division

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## AEROBIC SOIL METABOLISM STUDIES

### I. INTRODUCTION

#### A. Objective of the Standard Evaluation Procedure

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of the aerobic soil metabolism studies submitted by registrants in support of pesticide registration.

Aerobic soil metabolism studies are required by 40 CFR § 158.130 in support of registration of an end-use product intended for terrestrial use or forestry use (as defined by the Subdivision N Guidelines) and to support registration of a manufacturing-use product which may also be legally used to formulate such an end-use product. Section 162-1 in the Subdivision N Guidelines describes this study and provides a protocol for conducting it.<sup>1</sup>

Data on the aerobic soil metabolism of pesticides are used by the Agency to determine the nature and extent of formation of pesticide degradation products to which rotational crops and nontarget organisms will be exposed, and to facilitate assessment of potential disposal problems and which will be available for leaching to ground water.

#### B. General Theory of Aerobic Soil Metabolism

The reviewer should be acquainted with the physico-chemical and microbial soil processes causing pesticides to degrade and dissipate in the soil environment. The reviewer is directed to Appendix 1 for a brief description of those soil processes.

### II. THE SUBMITTED STUDY

#### A. Purpose

Aerobic soil metabolism studies should provide information on (1) the rate of degradation in soil; (2) identification of soil degradation products; (3) rate of formation and decline of the degradation products; and (4) a material balance. Information gained from this study is directly applied to designing and conducting field dissipation and accumulation studies. For example, it determines the degradation products one should analyze for in the field soil dissipation studies and to which degradation products rotational crops and nontarget organisms will be exposed.

## B. Study Design

The registrant's report should contain (1) a stated goal of the study; and (2) sufficient information on the test protocol (compound purity and type of compound used; complete characterization of soils; dose level and method of inoculation of soil; sufficient description of sampling frequency) and the analytical protocol (description of methods used for quantitative and qualitative analyses and reports on the quality control procedures used to ensure the validity of the study).

Types of information that the registrant should include in the report are listed in Appendices 2 and 3.

## III. THE EVALUATION PROCESS

### A. Determine the Need for the Study

The reviewer should initially determine whether the study is required under 40 CFR § 158.130. Normally, the study is required to support registration of each active ingredient in pesticide products intended for terrestrial or forestry end uses and for manufacturing-use products intended for use in formulating such end-use products.

### B. Read the Report

Reports of aerobic soil metabolism studies are first reviewed to determine if the following information is present:

1. Are the compound purity and site(s) of radiolabeling specified? If radiolabeling is used, complex molecules must be labeled in appropriate sites to allow each major component of the molecule to be monitored.

2. Is the complete characterization of soil(s) included [pH, moisture capacity, percent organic matter, bulk density, cation exchange capacity, and textural composition (percent sand, silt and clay) and textural class]?

3. Is the treatment rate and method of treatment of the soil described?

4. Were soil treatments replicated and sampled frequently?

5. Are the methods used to determine material balance described?

6. Are the methods used for quantitative and qualitative analyses of the degraded compound and formation and decline of

the degradation products described?

7. Is the material balance determined?
8. Is the half-life calculated?
9. Are the raw data from which a half-life can be calculated included?

The reviewer should determine if there are data gaps within the study. Failure to provide adequate information may be sufficient for the reviewer to reject the study. In cases where considerable information is missing, the reviewer should make a detailed list of the deficiencies and omissions and not provide a detailed scientific review of the report at this time.

C. Prepare the Data Evaluation Record (DER)

After the reviewer has determined there are no data gaps which would cause the report to be rejected, the reviewer prepares a DER according to the Standard Format For Preparation of Environmental Fate Reviews.

1. Write the Technical Evaluation

The reviewer should use Appendices 2 and 3 as aids in this process. The technical evaluation should be prepared with the following points in mind:

- a. The test protocol should provide adequate information as to how and under what conditions the study was conducted. Consult Appendix 2.
- b. The analytical protocol should provide information on sensitivity and specificity of the analytical method(s) used and indicate how the results were determined. Consult Appendix 3.
- c. The material balance aids in determining the validity of the study. Is all or the major portion (90-95%) of the test chemical applied to the soil accounted for?
- d. The rate of degradation of the test material provides a half-life estimate of the parent compound. It answers the questions:
  - Does the test material degrade?
  - Is it persistent in the soil environment?

It also provides a measure of predicting the degradation rate under field conditions.

- e. It is essential that the report provide the identity of the soil degradation products of the test substance in order to answer the following questions:
  - To what does the test chemical degrade?
  - How extensive is degradation? Does it mineralize to inorganic compounds (e.g., CO<sub>2</sub>)?
  - Which compounds can be expected to occur and should be looked for in the field dissipation studies?
  - To which compounds will rotational crops and other nontarget organisms (e.g., aquatic organisms) be exposed?
- f. The rate of formation and decline of degradation products provides a half-life estimate for the degradation products. This answers the questions:
  - Are the degradation products persistent in the soil environment and thereby available for leaching to the water table?
  - At what rate do they decline?
- g. Quality control information provides assurance of the integrity of the study. This information answers the questions:
  - Were logbooks and record-keeping procedures maintained?
  - Were quality procedures maintained during sampling, storage, and analysis of soil samples? Were good laboratory practices followed?
  - Was soil for testing maintained in a manner to maintain viable microbial populations?
- h. A degradation scheme of the test compound and degradation products can suggest which mechanisms contributed to the degradation.

## 2. Determine Study Acceptability

Were the stated goals of the study appropriate and clearly defined? Was the study conducted in a scientifically sound manner to accomplish those goals? If so, the reviewer then makes a determination as to the acceptability of the study and



considers whether the study, as it stands alone or in light of other studies (combined testing, surrogate studies, or waivers), supports the requested registration action.

If the study is deficient, a detailed description of the deficiencies and recommendations on how to rectify the deficiencies is prepared and included in the DER.

3. Determine Need for Deferral/Referral to Other HED Branches

If the reviewer concludes that (1) the test chemical or its degradates has/have a potential for reaching ground water due to its/their persistence, or (2) residues may occur in rotational crops due to their persistence, or (3) there may be exposure to other nontarget organisms due to persistence, then the Toxicology, Residue Chemistry, and/or Ecological Effects Branches may have to be notified. Final decision on the need for deferral/referral is to be made after the evaluation of the other environmental fate studies.

4. Make Regulatory Determination

Based on the technical evaluation, the reviewer determines whether the study satisfies the data requirement for an aerobic soil metabolism study as listed in 40 CFR § 158.130.

## APPENDIX 1

### General Theory

Pesticide products reaching the soil may either decompose completely to inorganic compounds (e.g.,  $\text{CO}_2$ ), be altered in varying degrees and become part of the soil complex, or remain intact in the soil ecosystem. In all cases, residues may be available for uptake by rotational crops and exposure to non-target organisms. Degradation products may become important when their rate of formation exceeds their rate of decomposition.

Numerous factors are known to influence fate and behavior of pesticides in the soil system. These factors are basically either chemical (i.e., non-biological) or microbial (biological) degradation. Usually these two processes work in conjunction.<sup>2,3</sup> However, where the influence of one stops and the other begins is not well defined. The most complex process by which pesticides are degraded in soils involves microbial utilization of the pesticide as an energy source.<sup>4</sup> The aerobic soil metabolism study is designed to measure degradation of the test compound from biological degradation due to microorganisms in the soil complex and from the soil-associated physico-chemical processes.

Microorganisms comprise a large fraction of the living biomass in soil - up to 80% when soil algae are included.<sup>5</sup> However, they are not all active under the same conditions. Microbial degradation in soil has been viewed as a process in which organisms adapt to the chemical and use it as a preferred food source.<sup>6</sup> A variety of organisms which are capable of using pesticides as the sole energy source have been identified. It is reported that microbial species belonging to 16 genera of bacteria, 2 of actinomycetes and 13 of fungi have been identified as being able to degrade 20 of the commonly used herbicides.<sup>7</sup> It appears, however, that microbial degradation of most agricultural chemicals at low concentrations applied to soil occurs primarily via cometabolism by soil organisms using soil organic matter as their main source of energy.<sup>6</sup>

Soil microorganisms can decompose most synthetic organic soil additives as well as the natural soil organics, but there are some limitations. Some synthetic organic chemicals involve unusual molecular structures to which organisms may not be well adapted.<sup>8</sup> The action of organisms on organic compounds is primarily enzymatic. Enzymes are abundant in soil.<sup>9</sup> Microbial-associated chemical reactions can include hydrolysis, oxidation ring cleavage, and dehalogenation, all of which contribute to ultimate formation of  $\text{CO}_2$  from the chemical in question. Where some microorganisms leave off in degradation of a chemical, others may begin. The reader is directed to additional literature on microbial activity in soil and on the biochemistry of living systems and their

components in soil (in particular, books edited by Gray and Parkinson<sup>10</sup> and McLaren and Peterson<sup>11</sup>).

There are numerous soil-associated physico-chemical reactions. Hydroxylation and oxidation are common soil chemical reactions.<sup>4</sup> Less is known of other mechanisms (reduction, isomerization, and free-radical reactions).

All the soil-associated chemical reactions are initiated through water acting as the medium of reaction, or reactant, or as both. These chemical reactions may be catalyzed by clay, metal oxides, metal ions, or extracellular enzymes.<sup>4</sup> The organic matter fraction of the soil can play a major role in the chemical degradation of pesticides in providing reactive functional groups<sup>12, 13</sup> as well as by retaining the molecule (adsorption) which allows these processes to take place.<sup>14</sup>

Both biodegradation and soil physico-chemical degradation are affected by soil pH. For example, microbial oxidation is most rapid between pH 6 and pH 8.<sup>14</sup> Soil water is seldom neutral and its pH range may vary from strongly acidic (pH 3) to strongly alkaline (pH 10.5).<sup>15</sup> A number of pesticides will hydrolyze rapidly under aqueous acidic and alkaline conditions that can be found in soil. For further information see the discussion in the Standard Evaluation Procedure for Hydrolysis Studies.

## APPENDIX 2

### Information to be Included in the Report

Section 162-1 in the Subdivision N Guidelines<sup>1</sup> describes this study and gives a protocol for conducting this study. Also, Section 160.5 in the Subdivision N Guidelines<sup>1</sup> describes general reporting and evaluation requirements for this study.

#### A. Information To Be Included

1. Dates on which the study began and ended;
2. Name and address of the laboratory or institution performing the test;
3. Location where the test was performed;
4. Names of the principal investigators;
5. Signatures of each of the senior personnel responsible for the study;
6. Certification by the registrant that the report is a complete and unaltered copy of the report provided by the testing facility;
7. The report should identify the test substance and include the chemical name and purity of active ingredient, molecular structure, manufacturer, and lot and sample number(s) of the test substance(s), and properties of the test substance(s) [including physical state, pH] if not reported elsewhere;
8. Description of the soil source and soil characteristics;
9. A detailed report in tabular form of the residue data from the treated soil (graphs are often included to expand on the data given in tabular form);
10. A complete discussion of the results of the study which should include a discussion of the following:
  - a. Material balance;
  - b. Degradation rate and half-life estimate of the parent;
  - c. Rate of formation and decline of the degradation products;

d. Identity of residues occurring at levels of 0.01 ppm or greater;

e. Residue decline curves.

B. Detailed Discussion

1. The test substance.

The chemical to be tested must be chemically pure. The use of radiolabeled compounds is preferred. Carbon-14 is usually used; ring labeling is preferred to side-chain labeling since the radioactivity is usually less easily removed from the central ring positions. If the molecule is complex and consists of moieties that are easily separated, then radiolabeling in more than one position of the compound may be necessary.

Use of radiolabeled chemicals rather than non-labeled ones allows: (1) the degradation process to be followed at a much lower concentration and (2) easier determination of mass (material) balance. If non-radiolabeled compound is used, the study must be conducted with the technical or purer grade of the active ingredient(s).

Sometimes, initial concentrations of the test substance in soil exceeding the proposed use rate should be studied to permit measurement of the disappearance of the parent compound and identification of the major degradates formed.

2. The test soil.

The rate, type and degree of metabolism of the pesticide and its major degradates should be determined in a sandy loam or silt loam. A different soil may be used if representative of the soil at the intended sites. For example, celery is usually grown in a muck soil. Thus, to support such a use it may be necessary to conduct the study in muck soil. If the use covers a crop that is grown in various soil types with wide geographic distribution, then more than one soil type must be studied. For example, soybeans are grown in large geographical areas encompassing several distinct soil types. Here, it will be necessary to conduct the study in both a sandy loam and loamy clay soil.

There is no best way to collect and store soils for conducting this study.<sup>16</sup> The soil should be a collection of subsamples from the top layer of the field soil. The majority of the field microbial populations is located in the top layer of soil (the upper 14 centimeters).<sup>17</sup> This is the area where nutrient levels and oxygen availability are high.<sup>18</sup> The soil should not have received prior pesticide applications. If soil has received prior treatment of the same or similar type of compound, then the microbial

enrichment or adaptation to that type of compound may have occurred. Subsequent pesticide applications may then degrade more rapidly.<sup>15</sup>

As in most routine soil analyses<sup>19</sup>, the soil should be sifted through a 2 mm sieve. This removes extraneous debris which could adsorb the test compound thus affecting the results of the study. The soil should preferably be freshly acquired from a typical use area or have been maintained in such a manner that viable microbial populations are present in the soil. The soil should be stored in a clean, chemical-free environment. The soil may be dried to approximately 75% of the moisture level at 1/3 bar (Note: 1/3 (0.33) bar is a laboratory measure of the soil moisture at field capacity - the amount of water remaining in soil after excess water has been removed by force of gravity<sup>16</sup>). However, it is important the soil not become air-dry as that can adversely affect the microorganism populations present.<sup>16</sup>

Complete information on the soil class, textural characterization of the soil, soil pH, and percent organic matter is necessary to verify that the soil is representative of agricultural soils. Use of U.S. soils from typical use areas is preferred but if foreign soils are used, such data on soil class and textural classification are needed to indicate its similarity to U.S. agricultural soils from typical use areas. When foreign soils are used, additional studies conducted with U.S. soils and of sufficient duration will also be needed to provide assurance that any possible differences in microbial populations between the foreign and U.S. soils does not result in different patterns of degradation.

Since many reactions are pH sensitive, the nature of the soil pH reaction is an important consideration. The organic matter content is a measure of microbial viability, being the main energy source for soil microorganisms.

#### 4. Test procedures.

##### a. Study apparatus.

The use of closed incubation systems, either flasks with side-arms<sup>20</sup> or positive air flow manifold systems<sup>21</sup>, are recommended for this study. They allow for determination of mass (material) balance. However, their use may be omitted if the parent compound is not volatile or if labeled CO<sub>2</sub> and/or other volatile metabolites are not formed. Collection of volatiles is necessary for the material balance and serves to indicate that the test material ultimately mineralizes to CO<sub>2</sub> or that other volatile organic compounds are formed. If the reviewer notes that an open system was used and the mass balance does not approximate 100% recovery, the reviewer can suspect that volatiles were formed but not

trapped. The reviewer should request clarification of this fact from the registrant, if not given.

b. Treatment rate.

The concentration of the test substance should be at levels sufficient to permit measurement of the disappearance of parent compound and identification of major degradation products. The dose should be at the highest proposed field use rate. Separate studies at higher doses (5 to 10X) may be necessary for identification of degradation products.

c. Study conditions.

Soil samples should be taken and replicated sufficiently to provide interpretable data for kinetic analysis. The soil study should include untreated controls. Treated soil should be maintained at a constant temperature between 18 and 30°C that is most representative of the use area. The recommended soil moisture content is at a level of 75 percent of 0.33 bar moisture. These are the soil moisture conditions most conducive to metabolism by aerobic microorganisms and is a compromise of the unlimited variety of combinations of temperature and moisture levels found in the natural environment.

One hundred percent of one-third (0.33) bar soil moisture represents the upper limit of soil moisture for aerobic microbial activity (equivalent to field moisture capacity). The 75% of 0.33 bar is a safe moisture level still within the optimum range.<sup>16</sup> It is probably a moisture level more prevalent in soil than 100% of 0.33 bar. If soil is maintained at another soil moisture level, this level should also be reported relative to the theoretical moisture content at 75% of 0.33 bar. However, the soil moisture level should be within 10-12% of the level at 75% of 0.33 bar moisture.

d. Duration of the study.

Reaction kinetics of decomposition of pesticides are concerned primarily with the decline in concentration of the pesticide over time.<sup>4, 8, 23</sup> However, the Guidelines<sup>1</sup> also require information on the degradation products. Therefore, data are collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established or for one year, whichever comes first for terrestrial crop and non-crop uses and forestry uses. When greenhouse and domestic outdoor uses are involved, data are collected through two half-lives of the test substance or to six months duration, whichever comes first. Data over these lengths of time are necessary for kinetic analyses.

e. Sample collection

The Guidelines<sup>1</sup> recommend sampling soil at pretreatment, immediately post-treatment, at 1, 3, 7, and 14 days, and at 1, 2, 3, 4, 6, 9, and 12 months post-treatment. To obtain sound kinetic data, it has been suggested that there should be at least six sampling points spread out over three half-lives of the chemical.<sup>16</sup> Others have suggested that the reaction should be followed for at least 1-1/2 half-lives if accurate rate constants are to be obtained.<sup>8</sup> Exact distribution will depend on rate of breakdown. However, an adequate number of samples should be collected in the beginning of the incubation in the event rapid degradation takes place.

If trapping solutions are used, they should be sampled when the soil is sampled.

Soil samples should be analyzed as soon as possible after being taken. If samples are stored before extraction and analysis, it must be shown that the pesticide residues will not degrade under the storage conditions. Spiked samples should be maintained under identical conditions and extracted with treated samples unless preliminary data are available which show that additional degradation does not occur under the storage conditions.



APPENDIX 3

Analytical Data to be Submitted by the Registrant

A. Analytical Procedures

1. Analytical methods.

A full description of the analytical methods used in all steps of the analytical protocol must be submitted, including the following information:

- a. Name (and signature), title, organization, address and telephone number of the person(s) responsible for the planning and supervision/monitoring and laboratory procedures/analyses;
- b. Analytical method(s) title/designation/date;
- c. Source of analytical method(s) (e.g., Pesticide Analytical Manual (P.A.M), Vol. II, scientific literature, Company reports);
- d. Principles of the analytical procedure (description);
- e. Copy of the analytical method(s) detailing in stepwise fashion the procedures (extraction, clean-up, derivatization, determination, calculation of the magnitude of the residue);
- f. Reagents or procedural steps requiring special precautions (to avoid safety or health hazards, explain);
- g. Identification of the chemical species determined;
- h. Describe modifications, if any, of the analytical method(s);
- i. Extraction efficiency;
- j. Instrumentation [make/model, type/specificity of detectors, column(s) packing materials, size, gas carrier, flow rates, temperatures, limit of detection and sensitivity, calibration procedures, etc].
- k. Interference(s), if any;
- l. Confirmatory techniques [e.g., other column packings, detectors, etc.];
- m. Date(s) of sample taking, extraction and residue analyses;

- n. Sample identification (Coding and labeling information);
- o. Residue results (raw data, laboratory worksheets, stepwise calculation of residue levels, dilution factors, peak heights/areas, method correction factors applied [e.g., storage stability and method validation recovery values, standard curve(s) used, ppm found of "total" residues and of individual components if of special concern, range of residue values, representative chromatograms, spectra of control and treated samples]);
- p. Statistical treatments (of raw data);
- q. Other (any and all additional information the registrant/researcher considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and the means of calculating the residue results).

#### B. Method Validation

A full description of the method recovery validation procedures must be submitted and must include information on the following: the recovery level(s) of the test compounds from the soil (substrate) at various fortification level(s) using the residue analytical methodology; a validated method sensitivity level; results of the study and statistical tests applied; a stepwise presentation of the procedure for calculating percent recovery from the raw data; all the data/information necessary to independently verify the results; summary of data results; and conclusions drawn from the data results.

#### C. Quality Assurance

A complete description of the measures taken to ensure the integrity of the test and analytical protocols should include information on the following: logbooks and/or record-keeping procedures; representative instrument printouts (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology for residue analyses, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high quality glassware, solvents, and test compounds; minimal contamination; calibration and maintenance of instruments; good laboratory practices in handling the test substance(s).

#### D. Residue Analysis

- 1. Samples should be subdivided and analyzed as follows:

- a. Total soil residues

When  $^{14}\text{C}$  labeled parent compound is used, the soil will be combusted in an oxidizer and  $\text{CO}_2$  formed will be trapped in appropriate

solvents. This provides a preliminary material balance.

b. Extractable soil residues

Soil is extracted with appropriate solvents, filtered, and re-extracted if necessary. Exhaustive extraction methods are sometimes necessary when residues are not extracted by gentler means. The reviewer should determine that an appropriate extracting solvent was used in the study. The reader is directed to Chesters, et al.<sup>23</sup> for a general overview on the subject of pesticide extraction and analysis of soil without elaboration on specific procedures and to Hance and McKone<sup>24</sup> for specific procedures for herbicides.

Extractable residues are considered as those being immediately available for uptake by rotational crops, exposure to nontarget organisms and for leaching into the ground water. They are also available for further degradation.

c. Non-extractable residues

The post-extracted soil is combusted in an oxidizer and the CO<sub>2</sub> formed is trapped in appropriate solvent. Non-extractable residues are those that may, at some later time, become available for uptake by rotational crops or for exposure to nontarget organisms. They are also a measure of the soil binding potential of the test chemical and degradation products.

These three residue totals - total volatile residues, total extractable residues and the non-extractable residues (expressed as percent of the total applied) - make up the material balance. The material balance summed should ideally equal 100% of the amount of test chemical applied. Thus, the material balance is a factor in determining the validity of the study. Studies wherein the material balance does not account for a large percentage (85-95%) or accounts for greater than 105-115% of the amount of test chemical applied may be invalid and not useful in satisfying the data requirement.

2. Identification of Metabolites

The Guidelines<sup>1</sup> require that residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified when feasible. Thin-layer chromatography (TLC) of extracted residues with co-chromatography of known standards is adequate for tentative qualitative identification. Autoradiography of TLC plates provides a record for locating any labeled degradation products. Liquid chromatography (LC) or gas chromatography and mass spectroscopy (GLC/MS) analysis provides positive metabolite identification. Quantitative analysis can be either by LSC, LC or GLC. All analytical methods must be examined for their

1. TLC  
2. HPLC &  
GC/MS

specificity, sensitivity, and recovery.

Identification of metabolites is a major part of the aerobic soil metabolism study and involves most of the analytical resources. Metabolites found in the aerobic soil metabolism study are considered representative of those that will be found in the soil under actual field conditions although different levels may be found under field conditions. Knowing the identity of the degradation products aids in preparing a degradation scheme of the test chemical and analyzing the field soil samples.

### 3. Half-life Estimate

As mentioned earlier, the reaction kinetics of pesticide degradation in soil are concerned primarily with the decline in concentration of the pesticide with time. For pesticides that are not strongly sorbed to soil, rates of degradation approach first-order kinetics at low concentrations and zero-order at high concentrations. Since pesticides are usually applied to soil at low concentrations and are often strongly sorbed, the rates of most chemicals should approach first-order kinetics. That is, the concentration of the pesticide in soil (which is usually low compared to the other reacting materials in soil) determines the velocity of the reaction.<sup>25</sup> However, rates tend to decrease with time more than would be expected which suggest sorptive forces are still active in the soil.<sup>6</sup> The rate of loss is proportional to its concentration in the soil and can be expressed by the equation:

$$- \frac{dc}{dt} = Kc^n \quad (1)$$

where  $c$  = the concentration of the pesticide,  $K$  = the rate constant,  $t$  = time and  $n$  is the order of the reaction. For first order kinetics,  $n = 1$ , therefore,

$$- \frac{dc}{dt} = Kc \quad (2)$$

where  $c$  is the amount of pesticide present in soil at time  $t$ . Here, the first-order reaction means that the disappearance of the pesticide is proportional to the amount left in the soil.

The first order is most commonly used since it is the simplest to use. Assuming first-order kinetics, the pesticide's half-life (the time required for the concentration to become equal to one-half of the original concentration) can be calculated. The dissipation of most pesticides from soils can be considered as following a first-order reaction<sup>26</sup> at least over

a portion of the degradation curve.<sup>4, 8</sup> It is reported that, overall, the reaction kinetics involved in decomposition of pesticides follow mostly the zero-, first-, and second-order reaction systems.<sup>27</sup> It is doubtful that any one single rate equation will ever be found which is applicable to all or most pesticides in soil.<sup>4</sup> The half-life estimate based on the kinetic analysis of the data generated in the aerobic metabolism study becomes a measure of persistence of pesticides under field conditions. However, it should be noted<sup>25</sup> that data summarized<sup>8</sup> show that the relationships imply that the proportion of the chemical degraded with time decreases as the concentration of the chemical decreases. The rate at which the last traces of a chemical disappears can be very slow.<sup>25</sup>

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